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PATENT SPECIFICATION

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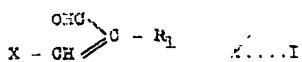
PROVISIONAL SPECIFICATION

Improvements in or relating to the Production of Cyanine Dye-stuffs and to the Sensitising of Photographic Emulsions

We, ILFORD LIMITED, a British Company, of 28, Boden Street, Ilford, in the County of Essex, do hereby declare the nature of this invention to be as follows:—

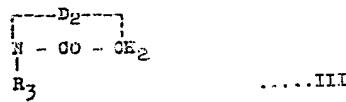
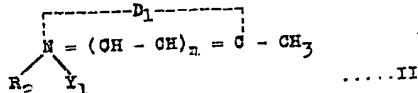
This invention relates to the production of cyanine dye-stuffs and particularly to the production of symmetrical dicarbo-cyanine dye-stuffs containing substituents in the polymethine chain. It further relates to the sensitising of photographic emulsions.

According to the present invention cyanine dye-stuffs are prepared by condensing a compound of the general formula I:—



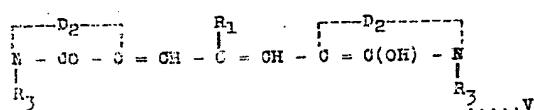
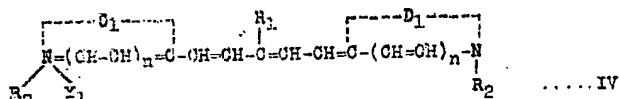
where R_1 is a nitrile (CN) or carboxylic ester (COOR) group and X is a thioether ($-\text{SR}$) or anil (NHR) group, R being a hydrocarbon group, with a heterocyclic nitrogen compound containing a reactive methylene group.

More particularly, according to this invention, the said heterocyclic compound 25 conforms to one or other of the following general formulae II and III:—



where R_2 is an alkyl, hydroxyalkyl or aralkyl group, Y_1 is an acid radicle, D_1 is the residue of a five-membered or six-membered heterocyclic ring, n is nought or one, R_3 is a hydrogen atom or an alkyl, aralkyl or aryl group and D_2 is the residue 35 of a heterocyclic nitrogen-keto-methylene nucleus.

Accordingly as compounds of formulae II or III are employed, so the products conform to formulae IV or V:—



The condensation may be effected in the presence of a base or in the presence of 45 an acid anhydride together with a base. A base such as pyridine is suitable, but

it is preferred to use a stronger base such as triethylamine or sodium acetate in conjunction with a carboxylic acid anhydride such as acetic anhydride.

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As already indicated R_1 may be a nitrile group or a carboxylic ester group. Examples of the latter are groups of the form $-COOR$ where R is an alkyl, e.g. 5 methyl, ethyl, propyl, butyl or higher alkyl group, an aralkyl group, e.g. benzyl or naphthylmethyl, or an aryl group, e.g. phenyl or naphthyl. R_2 may be any of the foregoing alkyl or aralkyl groups, or 10 may be a hydroxyalkyl group such as β -hydroxy ethyl or γ -hydroxy propyl. Where R_2 is an hydroxyalkyl group this will usually be acylated by the acid condensing agent so that R_2 in the product 15 will be an acyloxyalkyl group. R_3 , if not a hydrogen atom, may be any of the foregoing alkyl, aralkyl or aryl groups. X_1 may be any acid radicle, for example 20 halide (chloride, bromide, iodide), sulphate, sulphamate, perchlorate or p -toluenesulphonate.

X_1 may be the residue of any five-membered or six-membered heterocyclic ring system including thiazoles, oxazoles, selenazoles and their polycyclic homologues such 25 as those of the benzene, naphthalene, ace-naphthene and anthracene series; pyridine and its polycyclic homologues, such as quinolines and α - and β -naphthoquinolines; lepidines; indolines; diazines such as pyrimidines and quinazolines; diazoles (e.g. thio- $\beta\beta'$ -diazole); oxazolines, thiazolines and selenazolines. The 30 polycyclic compounds of these series may be substituted in the carbocyclic rings with one or more groups such as alkyl, aryl, amino, hydroxy, alkoxy and methylene dioxy groups, or by halogen atoms.

X_1 may be the residue of rhodanic acid (2-thio-4-keto-tetrahydrothiazole), oxo-rhodanic acid (2-thio-4-keto-tetrahydrothiazole) and the N-hydrocarbon substituted derivatives of such compounds. 35 oxindoles, pyrazole-5-ones, hydantoin, thio-hydantoin, pseudohydantoin and pseudothiohydantoin.

The initial starting compounds of 40 general formula I may be prepared by reacting a compound of the formula CH_2R_1 , i.e. acetonitrile or an acetic ester, with a formic ester (preferably ethyl formate) in the presence of powdered sodium. This yields the compound 45 $R_1-CH_2-CH_2-CO$ as its sodium salt. This product is then reacted with a mercaptan RS^H in the presence of dry hydrochloric acid or is reacted with aniline to produce the thioether or anil of the formula 50 $R_1-CH_2-CH_2-CO-X$. This latter compound is reacted further with a formic ester (preferably ethyl formate) and powdered sodium to yield a product of the formula I as required for use in the present 55 invention.

Many of the dyestuffs formed according to this invention are sensitising dyes for silver halide photographic emulsions.

The following illustrate the preparation of compounds of general formula I:— 70

A. PREPARATION OF α -CARBETHIOXY MALON-
DIALDEHYDE MONO ANIL.

10 parts of sodio formyl ethyl acetate were dissolved in 100 parts of water and added with stirring to a solution of 7 parts 75 of aniline in a mixture of 40 parts of acetic acid and 160 parts of water. The ethyl-anilinomethylene acetate was precipitated as a flocculent yellow solid. M.pt. 105°.

This preparation is analogous to that of v. Pechmann, Berichte der Deutschen Chemischen Gesellschaft, 25, 1047.

A suspension of 30 parts of the above ethyl-anilinomethylene acetate in 100 85 parts of dry ether and 11.7 parts of ethyl formate was added in portions to 3.62 parts of sodium powder under 200 parts of dry ether. A slight reaction ensued and afterwards the solution was refluxed 90 for 8 hours and then poured into water under an atmosphere of CO_2 . The water was ether extracted, the extracts dried over sodium sulphate and the ether removed by distillation. The product was 95 distilled under reduced pressure, b.pt. 197° at 8 mm. pressure to give an oil which solidified on cooling to a yellow crystalline mass.

B. PREPARATION OF ETHYL- α -FORMYL- β -ETHYLTHIO ACRYLATE. 100

14 parts of sodio formyl ethyl acetate and 25 parts of ethyl mercaptan were mixed together with 25 parts of dry ether and dry HCl gas passed through 105 the mixture for 2 hours with cooling. After being allowed to stand overnight, the solution was poured into dilute sodium carbonate solution, ether extracted, dried over sodium sulphate 110 anhydrous, and the ether evaporated. Distillation under reduced pressure yielded β -ethylthio ethyl acrylate. B.pt. 160—165° at 30 mm. pressure.

11 parts of the above β -ethylthioethyl 115 acrylate and 6 parts of ethyl formate were mixed with a little dry ether and reacted with 1.5 parts of sodium powder also under dry ether. After addition the mixture was heated for 24 hours and 120 poured into water under an atmosphere of carbon dioxide. The aqueous liquors were acidified with acetic acid, ether extracted, the extracts being washed with water, dried and the ether removed by 125 distillation. Distillation under reduced pressure yielded crude ethyl- α -formyl- β -

ethylthio acrylate. *M.pt.* 110-135° C. at 7 mm. pressure.

C. PREPARATION OF α -(*n*-PROPYL CARBETHOXY) MALONDIALDEHYDE MONO ANIL.

5 13 parts of sodium formyl-*n*-propyl acetate were dissolved in 66 parts of water and added with stirring to a solution of 8 parts of aniline in a mixture of 43 parts of acetic acid and 183 parts of water. The *n*-propyl-anilinomethylene acetate was precipitated as a slightly sticky yellow solid.

A suspension of 51 parts of the above *n*-propyl-anilinomethylene acetate in 100 parts of dry ether and 20 parts of ethyl formate was added in portions to 5 parts of sodium powder under 200 parts of dry ether. The mixture was refluxed for 8 hours and then poured into water under an atmosphere of CO_2 . The ether was then evaporated and the product filtered from the aqueous solution. It was a yellow solid, *m.pt.* 132°.

D. PREPARATION OF α -CYANO-MALON-DIALDEHYDE MONO ANIL.

25 30 parts of sodium formyl acetonitrile were dissolved in 267 parts of water and added with stirring to a solution of 30 parts of aniline in a mixture of 160 parts of acetic acid and 743 parts of water. The anilinomethylene acetonitrile was precipitated slowly as a yellow solid. *M.pt.* 119°.

A suspension of 7 parts of the above 35 anilinomethylene acetonitrile, 30 parts of dry ether and 4 parts of ethyl formate was added in portions to 1 parts of sodium powder under 100 parts of dry ether. After complete addition the mixture was refluxed for 4 days and then poured into water under an atmosphere of CO_2 . The ether was evaporated and the product filtered as a yellow solid. After crystallisation from ethyl alcohol 45 it melted at 183°.

The following Examples serve to illustrate the invention:-

EXAMPLE 1

BIS-2(3-ETHYL BENZTHIAZOLE)- γ -CARBETHOXY PENTAMETHINE CYANINE IODIDE.

50 Method (i). 10 parts of α -carbethoxy malondialdehyde mono anil, 30 parts of 2-methyl benzthiazole iodide and 200 parts of pyridine were heated together for 3 minutes when the solution turned dark red. 6 parts of triethylamine were added with shaking and the solution allowed to cool before pouring into water. The dyestuff crystallised, was filtered 55 and recrystallised from methyl alcohol to give dark green crystals. *M.pt.* 230° with decomposition.

Method (ii). 2 parts of ethyl- α -formyl- β -ethylthio acrylate, 6 parts of 2-methyl benzthiazole and 15 parts of 65 pyridine were heated together for 15 minutes, during which time a rich blue colour was formed. This solution was poured into water when the dyestuff crystallised as blue-green crystals. These 70 were well washed, dried and recrystallised from methyl alcohol. *M.pt.* 230° with decomposition.

This dyestuff, when incorporated in a gelatino silver bromide emulsion, im- 75 parts a band of sensitivity extending to 6800 Å with a maximum at 6400 Å.

EXAMPLE 2

BIS-2-(1-ETHYL QUINOLINE)- γ -CARBETHOXY PENTAMETHINE CYANINE IODIDE. 80

10 parts of α -carbethoxy malondialdehyde mono anil, 30 parts of quinaldine ethiodide and 200 parts of pyridine were heated together for 3 minutes when the solution turned red-green. 3 parts of tri- 85 ethylamine were added and the solution refluxed for 30 minutes, during which time a green colour slowly appeared. The pyridine solution was poured into water when the dyestuff crystallised. Recrystallisation from methyl alcohol gave blue-green crystals. *M.pt.* 253° (decomposition).

This dyestuff, when incorporated in a gelatino silver bromide emulsion, im- 90 parts a band of sensitivity extending to 7200 Å with a maximum at 6900 Å.

EXAMPLE 3

BIS - 2 - (1,3,3-TRIMETHYL-INDOLEINE)- γ -CARBETHOXY PENTAMETHINE CYANINE 100 IODIDE.

10 parts of α -carbethoxy malondialdehyde mono anil, 30 parts of 2:3:3 trimethyl indoleine methiodide and 200 parts of pyridine were treated as in the 105 above Examples. The dyestuff was obtained as dark green-blue crystals upon dilution with water which, when recrystallised from methyl alcohol, melted 110 at 207° (decomposition).

EXAMPLE 4

BIS - 2(3- β -ACETOXYETHYL BENZTHIAZOLE)- γ -CARBETHOXY PENTAMETHINE CYANINE 115 IODIDE.

10 parts of α -carbethoxy malondialde- 115 hyde mono anil, 31.6 parts of 2-methyl benzthiazole β -hydroxy ethiodide and 100 parts of acetic anhydride were heated together for 2 minutes when the colour of the solution attained a deep red. The 120 solution was then cooled to 100°, 3 parts of triethylamine added with shaking, and the blue solution allowed to cool slowly. The dyestuff was obtained by precipita-

tion with ether, washing with water and subsequent treatment with acetone. The dark blue solid obtained melted at 110°.

EXAMPLE 5

BIS-(3- β -ACETOXYETHYL-5-CHLOR-BENZTHIAZOLE)- γ -CARBOXY PENTAMETHINE CYANINE IODIDE.

10 parts of α -carbethoxy malondialdehyde mono anil, 34 parts of 2-methyl-5-chlor-benzthiazole- β -hydroxy ethiodide and 100 parts of acetic anhydride were heated together and treated as in the above Example. The dyestuff isolated as previously was obtained as dark green 15 powder crystals. M.pt. 154°.

EXAMPLE 6

BIS-(3- β -ACETOXYETHYL BENZTHIAZOLE)- γ - α -PROPYL CARBOXY PENTAMETHINE CYANINE IODIDE.

20 2.05 parts of α - n -propyl carboxy malondialdehyde mono anil, 3.1 parts of 2-methyl-benzthiazole- β -hydroxy ethiodide and 30 parts of acetic anhydride were heated together for 5 minutes. The solution was then cooled to 100°, 1.5 parts 25 of triethylamine added with shaking, and the blue solution then cooled rapidly to room temperature. Excess ether was added to precipitate the dyestuff as a tar 30 which was washed with water and then treated with acetone to give the crystalline dyestuff. This was recrystallised from methyl alcohol to give dark blue-green crystals. M.pt. 150° (decomposition).

This dyestuff, when incorporated in a gelatino silver bromide emulsion, imparts a weak band of sensitivity extending to 3300 Å with a maximum at 6500 Å.

EXAMPLE 7

BIS-(3- β -ACETOXYETHYL QUINOLINE)- γ - n -PROPYL CARBOXY PENTAMETHINE CYANINE IODIDE.

2.83 parts of α - n -propyl carboxy 45 malondialdehyde mono anil, 3.1 parts of quinoline- β -hydroxy ethiodide and 30 parts of acetic anhydride were heated together and 1.5 parts of triethylamine added. The procedure was similar to that 50 of the previous Example. The dyestuff was obtained, after crystallisation from methyl alcohol, as dark blue-green crystals. M.pt. 124° (decomposition).

EXAMPLE 8

BIS-2(3-ETHYL BENZTHIAZOLE)- γ -CYANO 55 PENTAMETHINE CYANINE IODIDE.

1.7 parts of α -cyano-malondialdehyde mono anil, 6 parts of 2-methyl benzthiazole ethiodide and 40 parts of acetic anhydride were heated together for 5 minutes, during which time the colour of the solution deepened to dark red. 1.6 parts of triethylamine were then added, and after another 3 minutes' refluxing, during which time a blue colour appeared, 60 the solution was cooled and the dyestuff filtered. When recrystallised from methyl alcohol it was obtained as dark brown crystals with a green reflex. M.pt. 268° (decomposition).

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This dyestuff, when incorporated in a gelatino silver bromide emulsion, imparts a weak band of sensitivity extending to 6600 Å with a maximum at 6350 Å.

EXAMPLE 9

 α , γ -BIS-(3-ETHYL-2-THIO-4-KETO-TETRAHYDROTHIAZOLE)- β -CYANO PROPENE.

1.7 parts of α -cyano-malondialdehyde mono anil, 5.2 parts of N-ethyl rhodanic acid and 40 parts of acetic anhydride were 80 heated together for 5 minutes. 1.4 parts of triethylamine were then added and heating continued for 15 minutes, during which time the dye colour (dark green-blue) gradually appeared. The solution 85 was cooled and the dyestuff filtered. Recrystallisation from methyl alcohol gave blue crystals with a bright reflex. M.pt. 220° (decomposition).

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EXAMPLE 10

BIS-(3- β -ACETOXYETHYL BENZTHIAZOLE)- γ -CYANO PENTAMETHINE CYANINE IODIDE.

1.7 parts of α -cyano malondialdehyde mono anil, 6.12 parts of 2-methyl benzthiazole- β -hydroxy ethiodide and 30 parts 95 of acetic anhydride were heated together for 5 minutes, 1 part of triethylamine added, and the solution refluxed for a further 3 minutes. The dyestuff was filtered, after cooling the solution, and 100 recrystallised from methyl alcohol when it was obtained as dark blue crystals. M.pt. 243° (decomposition).

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Dated this 13th day of May, 1948.

V. G. LAFENT,
Chartered Patent Agent.

COMPLETE SPECIFICATION

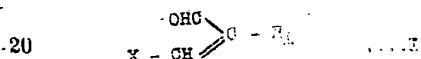
Improvements in, or relating to the Production of Cyanine Dyes and to the Sensitising of Photographic Emulsions

We, ILFORD LIMITED, a British Company, of 23, Roden Street, Ilford, in the County of Essex, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

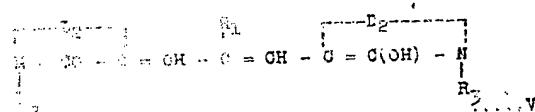
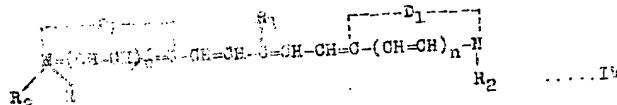
This invention relates to the production 10 of cyanine dyestuffs and particularly to the production of symmetrical dicarbo-cyanine dyestuffs wherein the substituents in the polymethylene chain. It further relates to the sensitizing of photographic emulsions.

15 emulsions.

According to the present invention cyanine dyestuffs are prepared by condensing a compound of the general formula I:—



where R₁ is a nitrile (R₁N≡C) a carboxylic ester (COOR₁) group and R₂ is a thioether (—SR₂) or anil (C₆H₅NR₂) group. R₃ is a hydrocarbon group, e.g. an alkyl group of 25 1 to 4 carbon atoms or an aryl group of 6 to 10 carbon atoms with a heterocyclic

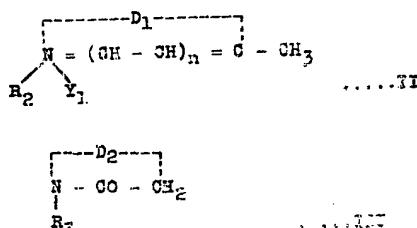


The condensation may be effected in the presence of a base or in the presence of an acid anhydride together with a base. A base such as pyridine is suitable, but it is preferred to use a strong base such as triethylamine or sodium acetate in conjunction with a carboxylic acid anhydride such as acetic anhydride.

As already indicated R_1 may be a nitrile group or a carboxylic ester group. Examples of the latter are groups of the form $-COOR$ where R is an alkyl, e.g. 60 methyl, ethyl, propyl, etc., or an aryl alkyl group, an aryl group, e.g. benzyl or naphthylmethyl, or an aryl group, e.g. phenyl or naphthyl. R_2 may be any of

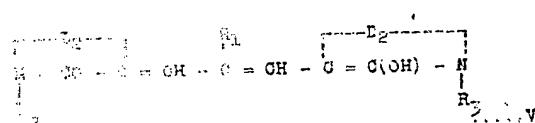
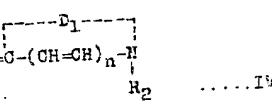
nitrogen compound containing a reactive methylene group.

More particularly, according to this invention, the said heterocyclic compound conforms to one or other of the following general formulae II and III:—



where R_2 is an alkyl, hydroxylalkyl or 35 aralkyl group, Y_1 is an acid radicle, D_1 is the residue of a five-membered or six-membered heterocyclic ring, n is nought or one, R_3 is a hydrogen atom or an alkyl, aralkyl or aryl group and D_2 is the residue 40 of a heterocyclic nitrogen-keto-methylene nucleus.

Accordingly as compounds of formulæ II or III are employed, the products conform to formulæ IV or V:—



the foregoing alkyl or aralkyl groups, or may be a hydroxyalkyl group such as β -hydroxy ethyl or γ -hydroxy propyl. Where R_2 is an hydroxyalkyl group this will usually be acylated by the acid condensing agent so that R_2 in the product will be an acyloxyalkyl group. R_2 , if not a hydrogen atom, may be any of the foregoing alkyl, aralkyl or aryl groups.

Y_1 may be any acid radicle, for example halide (chloride, bromide, iodide), sulphate, sulphinate, perchlorate or 2-75 toluene sulphonate.

D_1 may be the residue of any five-membered or six-membered heterocyclic ring system including thiazoles, oxazoles, selen-

azoles and their polycyclic homologues such as those of the benzene, naphthalene, ace-naphthalene and anthracene series; pyridine and its polycyclic homologues, such as 5 quinoline and α - and β -naphthoquinolines; imidazoles; indolenines; diazines such as pyrimidines and quinazolines; diazoles (e.g. thio- $\beta\beta'$ -diazole); oxazolines, thiazolines and selenazolines. The 10 polycyclic compounds of these series may be substituted in the carbocyclic rings with one or more groups such as alkyl, aryl, amino, hydroxy, alkoxy and methylene dioxy groups, or by halogen 15 atoms.

D_2 may be the residue of rhodanic acid (2-thio-4-keto-tetrahydrothiazole), oxazolidine acid (2-thio-4-keto-tetrahydro-oxazole) and the N-hydrocarbon substituted derivatives of such compounds, 20 oxadiazoles, pyrazole-5-ones, hydantoin, thio-hydantoin, pseudohydantoin and pseudothiohydantoin.

The initial starting compounds of 25 general formula I may be prepared by reacting a compound of the formula $\text{C}_2\text{H}_5\text{R}$, i.e. acetonitrile or an acetic ester, with a formic ester (preferably ethyl formate) in the presence of powdered sodium. This yields the compound $\text{R}-\text{CH}_2-\text{CH}_2\text{CO}$ as its sodium salt. This product is then reacted with a mercaptan (RSH) in the presence of dry hydrochloric acid, and is treated with aniline to produce 30 the thioether or sulfin of the formula $\text{R}-\text{CH}_2-\text{CH}_2-\text{SR}$. This latter compound is reacted further with a formic ester (preferably ethyl formate) and powdered sodium to yield a product of the formula 35 I as required, for use in the present invention.

The reaction is preferably effected using one molecular equivalent of the compound of formula I with substantially two mole- 40 cul equivalents of the compound of formic acid, i.e. by heating the reagents together conveniently at the boiling point of the formic acid anhydride employed, e.g. 130° to 150°.

Many of the products formed according 45 to this reaction are sensitising dyes for silver salt photographic emulsions.

The following illustrate the preparation of compounds of general formula I:—

55 A. PREPARATION OF α -CARBETHOXY MALON- OXYCARBONYL MONO ANIL.

15 parts of sodium formyl ethyl acetate were dissolved in 100 parts of water and added with stirring to a solution of 7 parts 50 of aniline in a mixture of 40 parts of acetic acid and 160 parts of water. The esterification and cleavage acetate was performed as a fluorescent yellow solid. M.p. 130°.

This preparation is analogous to that of 55 v. Pechmann, Berichte der Deutschen Chemischen Gesellschaft, 25, 1047.

A suspension of 30 parts of the above ethyl-anilinomethylene acetate in 100 parts of dry ether and 11.7 parts of ethyl 70 formate was added in portions to 3.62 parts of sodium powder under 200 parts of dry ether. A slight reaction ensued and afterwards the solution was refluxed for 8 hours and then poured into water 75 under an atmosphere of CO_2 . The water was ether extracted, the extracts dried over sodium sulphate and the ether removed by distillation. The product was distilled under reduced pressure, b.p.t. 80 197° at 8 mm. pressure to give an oil which solidified on cooling to a yellow crystalline mass.

B. PREPARATION OF ETHYL- α -FORMYL- β - ETHYLTHIO ACRYLATE. 85

14 parts of sodium formyl ethyl acetate and 25 parts of ethyl mercaptan were mixed together with 25 parts of dry ether, and dry HCl gas passed through the mixture for 2 hours with cooling. 90 After being allowed to stand overnight, the solution was poured into dilute sodium carbonate solution, ether extracted, dried over sodium sulphate anhydrous, and the ether evaporated. 95 Distillation under reduced pressure yielded β -ethylthio ethyl acrylate. B.p.t. 160—165° at 30 mm. pressure.

11 parts of the above β -ethylthioethyl acrylate and 6 parts of ethyl formate 100 were mixed with a little dry ether and reacted with 1.5 parts of sodium powder also under dry ether. After addition the mixture was heated for 24 hours and poured into water under an atmosphere 105 of carbon dioxide. The aqueous liquors were acidified with acetic acid, ether extracted, the extracts being washed with water, dried and the ether removed by distillation. Distillation under reduced 110 pressure yielded crude ethyl- α -formyl- β -ethylthio acrylate. B.p.t. 110—135° C. at 7 mm. pressure.

C. PREPARATION OF α -(*n*-PROPYL CARB- OXY) MALONITRALEHYDE MONO ANIL. 115

13 parts of sodium formyl-*n*-propyl acetate were dissolved in 66 parts of water and added with stirring to a solution of 8 parts of aniline in a mixture of 43 parts of acetic acid and 186 parts of 120 water. The *n*-propyl-anilinomethylene acetate was precipitated as a slightly sticky yellow solid.

A suspension of 51 parts of the above *n*-propyl-anilinomethylene acetate in 100 125 parts of dry ether and 20 parts of ethyl formate was added in portions to 5 parts

of sodium powder under 200 parts of dry ether. The mixture was stirred for 8 hours and then poured into water under an atmosphere of CO₂. The ether was then evaporated and the product filtered from the aqueous solution. It was a yellow solid, m.p. 132°.

D. PREPARATION OF α -CARBETHOXY-MALON-DIALDEHYDE MONO ANIL.

10 30 parts of sodium formyl acetonitrile were dissolved in 267 parts of water and added with stirring to a solution of 30 parts of aniline in a mixture of 100 parts of acetic acid and 746 parts of water.

15 The anilinomethylene acetonitrile was precipitated slowly as a yellow solid. M.p. 119°.

A suspension of 7 parts of the above anilinomethylene acetonitrile, 50 parts of dry ether and 4 parts of methyl formate was added in portions to 11 parts of sodium powder under 100 parts of dry ether. After complete addition the mixture was refluxed for 4 days and then 20 poured into water under an atmosphere of CO₂. The ether was evaporated and the product filtered as a yellow solid. After crystallisation from ethyl alcohol it melted at 183°.

25 30 The following Examples serve to illustrate the invention: -

EXAMPLE 1

BIS-2(3-ETHYL BENZTHIAZOLE)- γ -CARBETHOXY PENTAMETHINE CYANINE IODIDE.

35 Method (i). 10 parts of α -carbethoxy malondialdehyde mono anil, 30 parts of 2-methyl benzthiazole-3-hydroxy ethicidide and 100 parts of pyridine were heated together for 3 minutes when the solution turned 40 dark red. 6 parts of triethylamine were added with shaking and the solution allowed to cool before pouring into water. The dyestuff crystallised, was filtered and recrystallised from methyl alcohol 45 to give dark green crystals. M.p. 220° with decomposition.

Method (ii). 2 parts of ethyl-formyl- β -ethylthio ethicidide, 1 part of 2-methyl benzthiazole-3-hydroxy ethicidide and 50 pyridine were heated together for 15 minutes, during which time a rich blue colour was formed. The solution was 55 poured into water where the dyestuff crystallised as blue-green crystals. These were well washed, dried and recrystallised from methyl alcohol. M.p. 213° with decomposition.

This dyestuff, when incorporated in a gelatino silver bromide emulsion, 60 parts a band of sensitivity extending to 6800 Å with a maximum at 6400 Å.

EXAMPLE 2

BIS-2(1-ETHYL QUINOLINE)- γ -CARBETHOXY PENTAMETHINE CYANINE IODIDE.

10 parts of α -carbethoxy malondialdehyde mono anil, 30 parts of quinaldine ethioidide and 200 parts of pyridine were heated together for 3 minutes when the solution turned red-green. 6 parts of triethylamine were added and the solution 70 refluxed for 30 minutes, during which time a green colour slowly appeared. The pyridine solution was poured into water when the dyestuff crystallised. Recrystallisation from methyl alcohol gave blue-green crystals. M.p. 252° (decomposition).

This dyestuff, when incorporated in a gelatino silver bromide emulsion, 75 parts a band of sensitivity extending to 80 7200 Å with a maximum at 6900 Å.

EXAMPLE 3

BIS - 2 - (1.3.8-TRIMETHYL-INDOLENINE)- γ -CARBETHOXY PENTAMETHINE CYANINE IODIDE.

10 parts of α -carbethoxy malondialdehyde mono anil, 30 parts of 2:3:3-trimethyl indolenine methiodide and 200 parts of pyridine were reacted as in the above Examples. The dyestuff was obtained as dark green-blue crystals upon dilution with water which, when recrystallised from methyl alcohol, melted at 207° (decomposition).

EXAMPLE 4

BIS - 2(3- β -ACETOXYETHYL BENZTHIAZOLE)- γ -CARBETHOXY PENTAMETHINE CYANINE IODIDE.

10 parts of α -carbethoxy malondialdehyde mono anil, 31.6 parts of 2-methyl 100 benzthiazole β -hydroxy ethicidide and 100 parts of acetic anhydride were heated together for 2 minutes when the colour of the solution attained a deep red. The solution was then cooled to 100°, 1 parts 105 of triethylamine added with shaking and the blue solution allowed to cool slowly. The dyestuff was obtained by precipitation with ether, washing with water and subsequent treatment with acetone. The 110 dark blue solid obtained melted at 110°.

EXAMPLE 5

BIS-2(3- β -ACETOXYETHYL-5 - CHLOR-BENZ-THIAZOLE)- γ -CARBETHOXY PENTAMETHINE CYANINE IODIDE.

10 parts of α -carbethoxy malondialdehyde mono anil, 34 parts of 2-methyl-5-chlor-benzthiazole-3-hydroxy ethicidide and 100 parts of acetic anhydride were heated together and treated as in the 120 above example. The dyestuff isolated as previously was obtained as dark green powdery crystals. M.p. 164°.

EXAMPLE 6

BIS-2-(3- β -ACETOXYETHYL BENZTHIAZOLE)- γ -(*n*-PROPYL-CARBOXY) PENTAMETHINE CYANINE IODIDE.

5 2.50 parts of *n*-*n*-propyl carboxy malondialdehyde mono anil, 3.1 parts of 2-methyl benzthiazole- β -hydroxy ethiodide and 20 parts of acetic anhydride were heated together for 3 minutes. The solution was then cooled to 100°, 1.5 parts of triethylamine added with shaking, and the blue solution then cooled rapidly to room temperature. Excess ether was added to precipitate the dyestuff as a tar which was washed with water and then treated with acetone to give the crystalline dyestuff. This was recrystallised from methyl alcohol to give dark blue-green crystals. M.pt. 150° (decomposition).

26 This dyestuff, when incorporated in a gelatine silver bromide emulsion, imparts a weak band of sensitivity extending to 6500 Å with a maximum at 6500 Å.

EXAMPLE 7

BIS-2-(3- β -ACETOXYETHYL QUINOLINE)- γ -(*n*-PROPYL-CARBOXY) PENTAMETHINE CYANINE IODIDE.

30 2.50 parts of *n*-*n* propyl carboxy malondialdehyde mono anil, 3.1 parts of quinolined- β -hydroxy ethiodide and 20 parts of acetic anhydride were heated together and 1.5 parts of triethylamine added. The procedure was similar to that of the previous example. The dyestuff was obtained after crystallisation from methyl alcohol, as dark blue-green crystals. M.pt. 152° (decomposition).

EXAMPLE 8

40 BIS-2-(3-*ETHYL* BENZTHIAZOLE)- γ -CYANO PENTAMETHINE CYANINE IODIDE.

45 1.7 parts of *n*-cyano-malondialdehyde mono anil, 3 parts of 2-methyl benzthiazole- β -ethiodide and 40 parts of acetic anhydride were heated together for 3 minutes. During this time the colour of the solution deepened to dark red. 1.6 parts of triethylamine were then added, and after another 3 minutes' refluxing, 50 during which time a blue colour appeared, the solution was cooled and the dyestuff precipitated. When recrystallised from methyl alcohol it was obtained as dark brown crystals with a green reflex. M.pt. 268° (decomposition).

55 This dyestuff, when incorporated in a gelatine silver bromide emulsion, imparts a weak band of sensitivity extending to 6300 Å with a maximum at 6350 Å.

EXAMPLE 9

60 4,4'-BIS-(3-*ETHYL*-2-*KETO*-4-*KETO*-TETRA-THIAETHIOLYL)- γ -CYANO PROPENE.

65 1.7 parts of *n*-cyano-malondialdehyde mono anil, 3 parts of N-ethyl rhodanine and 30 parts of acetic anhydride were

heated together for 5 minutes. 1.4 parts of triethylamine were then added and heating continued for 15 minutes, during which time the dye colour (dark green-blue) gradually appeared. The solution 70 was cooled and the dyestuff filtered. Recrystallisation from methyl alcohol gave blue crystals with a bright reflex. M.pt. 230° (decomposition).

EXAMPLE 10.

BIS-2-(3- β -ACETOXYETHYL BENZTHIAZOLE)- γ -CYANO PENTAMETHINE CYANINE IODIDE.

75 1.7 parts of *n*-cyano malondialdehyde mono anil, 6.12 parts of 2-methyl benzthiazole- β -hydroxy ethiodide and 30 parts 80 of acetic anhydride were heated together for 5 minutes. 1 part of triethylamine added, and the solution refluxed for a further 3 minutes. The dyestuff was filtered, after cooling the solution, and 85 recrystallised from methyl alcohol when it was obtained as dark blue crystals. M.pt. 243° (decomposition).

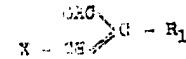
EXAMPLE 11

BIS-2-(3-*ETHYL* BENZSELENAZOLE)- γ -CARBOETHOXY PENTAMETHINE CYANINE IODIDE.

90 19.6 parts of 2-methyl benzselenazole and 18.6 parts of methyl-*p*-toluene sulphonate were fused at 100° C. for 3 hours, 10 parts of *n*-carboxy malondialdehyde 95 mono anil and 20 parts of acetic anhydride were added, and the mixture boiled for 30 minutes. Excess triethylamine was then added with cooling, whereupon the dyestuff was formed and precipitated from 100 the blue solution as a tar. This on treatment with acetone gave green crystals of the dyestuff, m.pt. 150° C. (with decomposition).

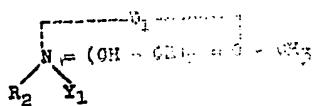
Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the preparation of 110 cyanine dyestuffs which comprises condensing a compound of the general formula:—



where R_2 is a nitrile (CN) or carboxylic 115 ester (COOR) group, and X is a thioether (SR) or anil (NHR) group, R being a hydrocarbon group, with a heterocyclic nitrogen compound containing a reactive methylene group.

2. Process according to claim 1 where in the heterocyclic compound containing a reactive methylene group is a compound of the general formula:—



where R is alkyl, aralkyl or hydroxy-alkyl, Y_1 is an acid radicle, D_1 is a residue of a five-membered or six-membered ring, and n is nought or one.

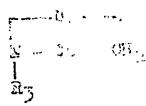
5. Process according to claim 1 or 2 wherein the reaction is effected by heating the reagents in the presence of a base.

10. Process according to any one of the preceding claims wherein the reaction is effected by heating the reagents in the presence of a carboxylic acid anhydride and a strong base.

15. Process according to claim 4 wherein in the anhydride employed is an acetic anhydride and the base is triethylamine.

20. Process according to any one of claims 2 to 5 wherein the residue D_1 is the residue of a benzthiazole, quinoline or indoleazine nucleus.

25. Process according to claim 3 wherein in the heterocyclic compound containing a reactive methylene group is a compound of the general formula:



wherein R_3 is a hydrogen or a methyl or an alkyl, aralkyl or aryl group, and R_1 is the residue of a heterocyclic nitrogen-keto-methylene ring.

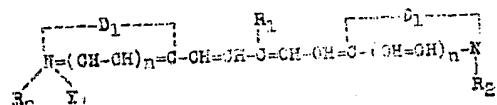
30. Process according to any one of the preceding claims wherein in the residue D_1 is the residue of a rhodanic acid anhydride.

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copies, price 3s 3d each (abroad) 2s. 1d. (abroad) may be obtained.

9. Process for the production of a cyanine dyestuff substantially as set forth in any one of the foregoing specific 35 Examples 1 to 11.

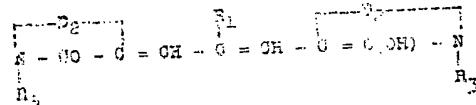
10. Cyanine dyestuffs wherever prepared or produced by any of the processes hereinbefore described and claimed.

11. A photographic emulsion containing in sensitising amount a dyestuff of the general formula:



where R_1 is a nitrile or carboxylic ester group, R_2 is an alkyl, aralkyl, hydroxy-alkyl or acyloxyalkyl group, Y_1 is an acid radicle, D_1 is a residue of a five-membered or six-membered ring, and n is nought or one.

15. A photographic emulsion containing in sensitising amount a dyestuff of the general formula:



where R_1 is a nitrile or carboxylic ester group, R_2 is a hydrogen atom or an alkyl, aryl or aralkyl group, and D_2 is the residue of a heterocyclic nitrogen-keto-methylene ring.

Dated this 6th day of May, 1970

V. GALLAHER,
Chartered Patent Agent.